Chemistry and Microphysics of the Troposphere: Global Emissions Inventories

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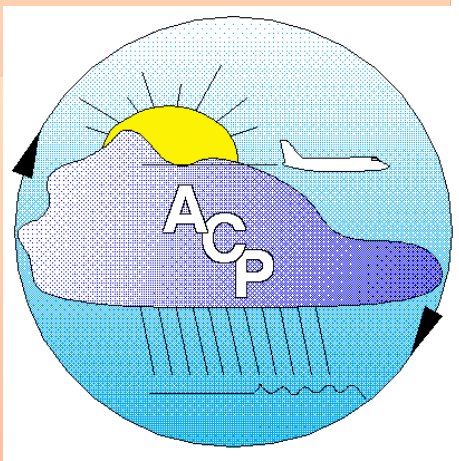


Anthropogenic Sulfur Emissions

★ **Collaborative effort with Canadian ORTECH Environmental under IGAC/GEIA.**

★ **Reference year: 1990.**

★ **Specifications**

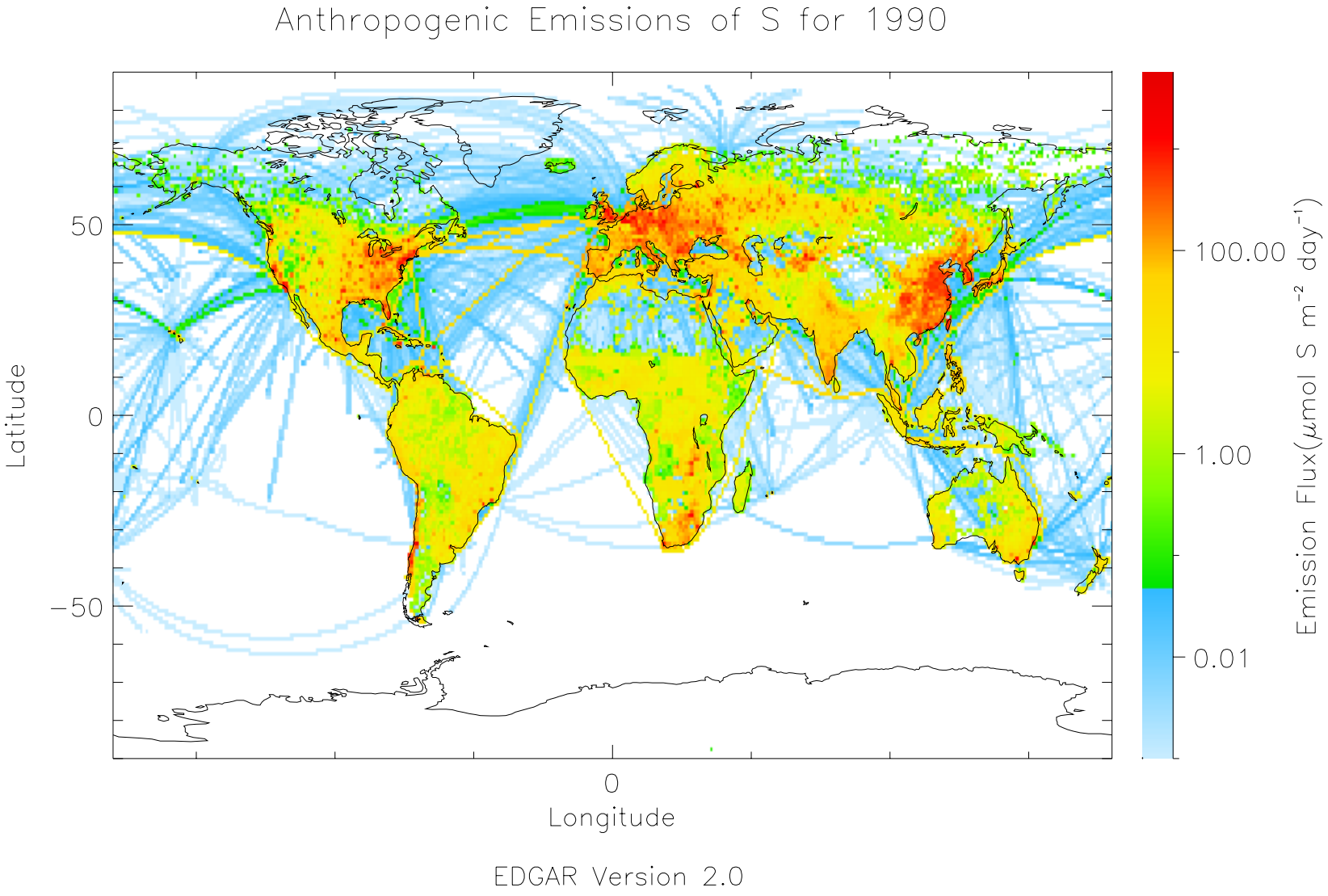
- **Global coverage.**
- **Seasonal.**
- **Total emissions by country and sectors.**
- **Major point sources separated from minor point sources and area sources.**
- **Emissions by sectors gridded to $1^{o} \times 1^{o}$.**
- **Emissions speciated to SO_2 and primary sulfate.**

Anthropogenic Sulfur Emissions

- ★ **Default inventory: EDGAR 1990 inventory, Olivier et al., 1995.**
- ★ **Regional inventories currently available:**
  - # **U. S.: USEPA inventories.**
  - # **Canada: AES inventories.**
  - # **Australia: F. Carnovale, personal communication.**
  - # **New Zealand: H. Plume, personal communication.**
  - # **Europe: CORINAIR.**
  - # **Asia: RAINS inventories.**
  - # **Russia: A.G. Ryaboshapko.**
  - # **Mexico: partial inventories available from:**
    - ▸ **Mexico Air Quality Research Initiative (Lead: DOE).**
    - ▸ **BRAVO (Lead: EPA).**
- ★ **Inventory available: fall 1999.**

Source Sectors for GEIA Anthropogenic SO_2 Inventory

Main source	Sector division	Source type
Power generation	Power generation	Major
Fuel use	Industry	Minor
	RCO	Area
	Incineration	Area
Transport	Road	Mobile
	Non-road	Mobile
	Air	Mobile
	Shipping	Mobile
Ind. processes	Iron & Steel	Major
	Copper	Major
	Lead	Major
	Zinc	Major
	Aluminum	Major
	Chemicals	Minor
	Cement	Major
	Pulp & paper	Minor
	Other	Minor
Landuse	Deforestation	Area
	Savannah	Area
	Agr. waste burning	Area


Anthropogenic Emissions of S for 1990
50
0
−50
Latitude
0
Longitude
100.00
1.00
0.01
Emission Flux(μmol S m⁻² day⁻¹)
EDGAR Version 2.0

Dimethyl Sulfide (DMS - CH_3SCH_3)

Relation to Climate

★ **CLAW Hypothesis**

- **Emissions of DMS can lead to global cooling opposing the greenhouse warming.**

★ **A postulated negative feedback mechanism:**

- **Greenhouse warming.**
- **Phytoplankton growth.**
- **DMS flux.**
- **Cloud formation.**
- **General cooling of surface temperatures.**

Oceanic Emissions of DMS

Background

★ Most phytoplankton species, ubiquitous in oceans, excrete DMS.

★ DMS production depends on phytoplankton growing conditions such as:

- # Light.
- # Upper ocean temperature.
- # Phytoplankton species.
- # Sea surface salinity.
- # Mixed layer depth.

★ Oxidized in the atmosphere to SO_2 and MSA.

★ Further oxidation of SO_2 to sulfate aerosol contributes to cloud condensation nuclei (CCN).

★ Estimated global emissions ~ 40 Tg S yr^{-1}, Andreae 1985.

Oceanic Emissions of DMS

Methodology

★ **General procedure.**

- # A database of measurements of the concentrations of DMS in surface ocean waters was compiled by Kettle et al (1996).
- # Applied the kriging technique to the data compiled by Kettle et al. to obtain gridded DMS concentrations in surface ocean waters.
- # Obtain global DMS fluxes to atmosphere by applying flux models of Liss & Merlivat (1986) and/or Wannikhof (1992).

Oceanic Emissions of DMS

Methodology

★ **Summary of Kettle et al. compilation**

9256 data points

Coverage — Extent (10^6 km^2)

- 4904 in Atlantic Ocean. — 74.56
- 3357 in Pacific Ocean. — 148.92
- 833 in Southern Ocean. — 57.89
- 162 in Indian Ocean. — 45.38

Source

- 8190 points contributed by scientists
- 1066 points digitized from publications etc.

Other parameters included:

- Aqueous dimethylsulfoniopropionate (DMSP)
- Particulate DMSP
- Sea surface temperature, sampling depth, etc.

Oceanic Emissions of DMS

Methodology

★ **Kriging**

- # A geostatistical procedure to estimate gridded values from a 2-D set of points.
- # Assumes spatial homogeneity, i.e, pattern of variation is similar at all locations on the surface.
- # An excellent linear unbiased estimator.
- # Assigns low weights to distant samples and vice versa.
- # Takes into account the relative position of the samples to each other as well as the area being examined.
- # Response of the grid point = $\sum$ (Weight * response of the spot point), where weight = 1/(distance from grid point to spot point, normalized for all the spot points).

Oceanic Emissions of DMS

Methodology

Spatial variation is quantified by the semi-variogram.

A semi-variogram is defined as *half* of the average squared difference between the two attribute values separated by a distance h (lag):

$$Y(h) = 1/2n \sum \{Z(x_i) - Z(x_i + h\}^2$$

- n is the number of pairs of sample points.
- h is the separation distance.
- Z are the attribute values.
- Y is the estimated spatial variation.

Uses optimum grid cell size for interpolation.

Oceanic Emissions of DMS

Methodology

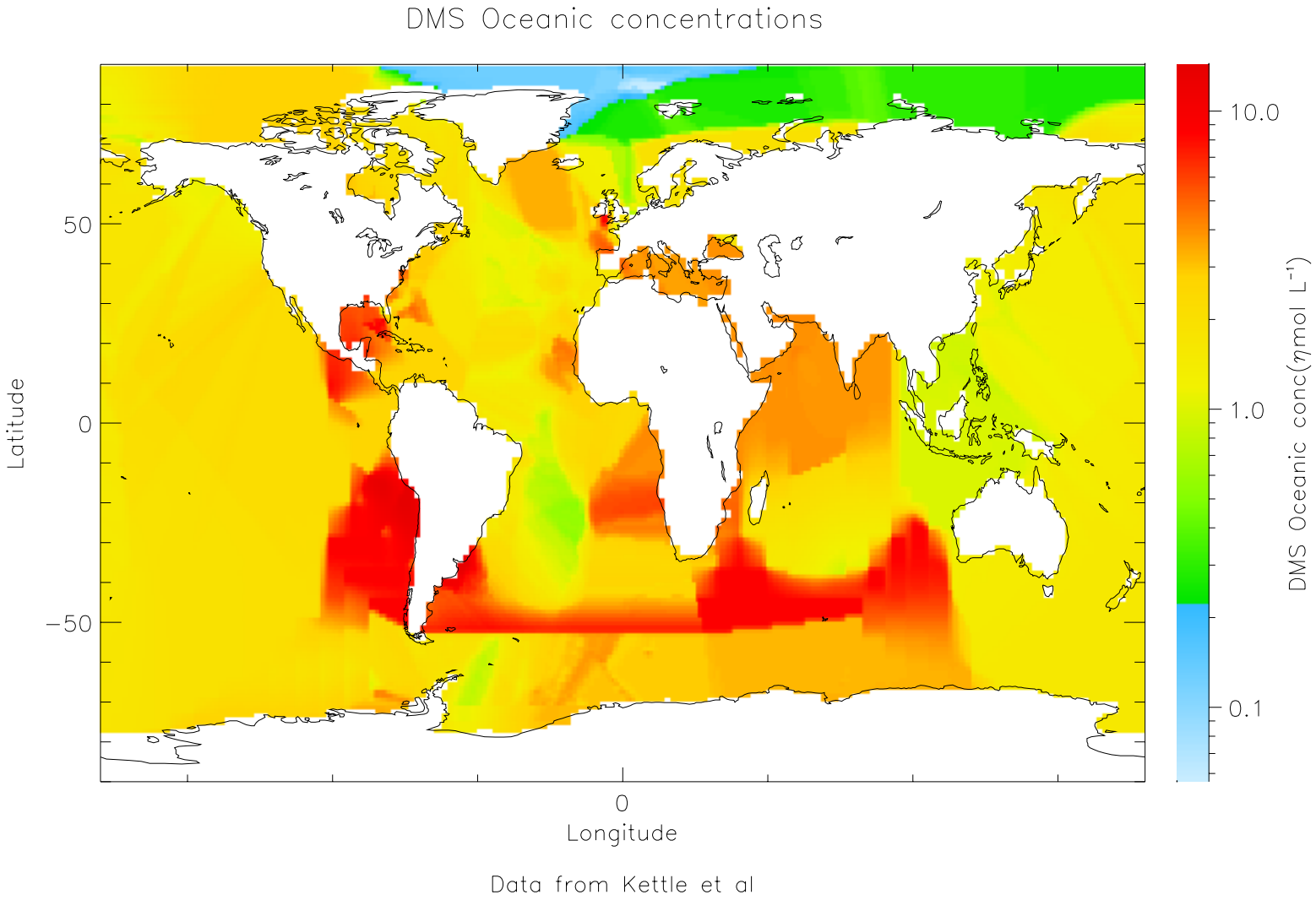
★ **Creation of the gridded DMS inventory for ACE-1**

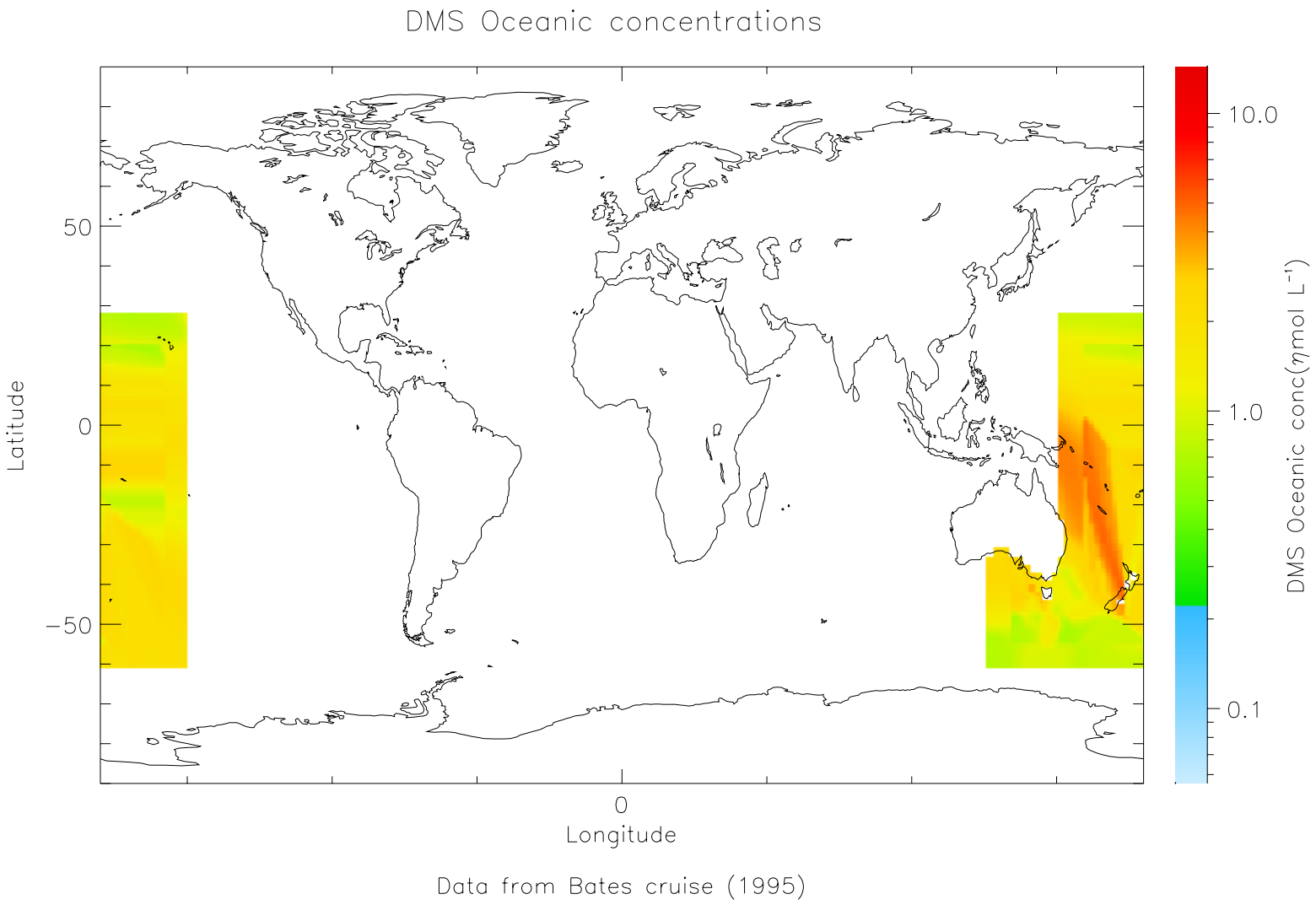
- For each of the four Oceanic areas in the Kettle compilation:
  - Extracted the surface ocean DMS concentrations for September to January.
  - Krigged the concentrations limiting the kriging domain by the extent of the respective ocean.
  - Merged and smoothed the four grids.
- Kriged Bates ACE-1 DMS surface ocean concentrations within ACE-1 experimental region.
- Replaced all the values within ACE-1 region in the global grid by the Bates ACE-1 grid. Smoothed concentrations at the boundaries.

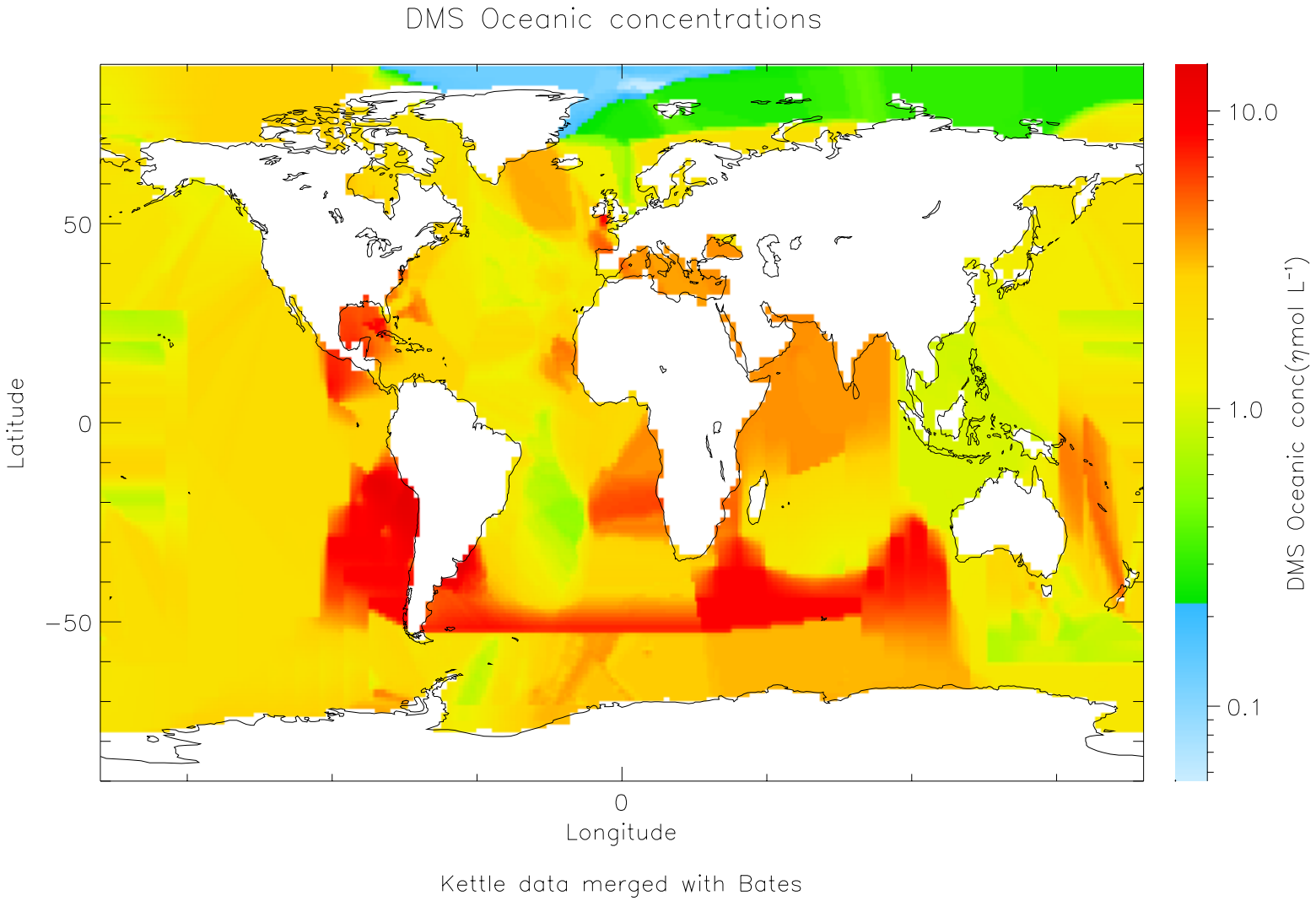
Oceanic Emissions of DMS

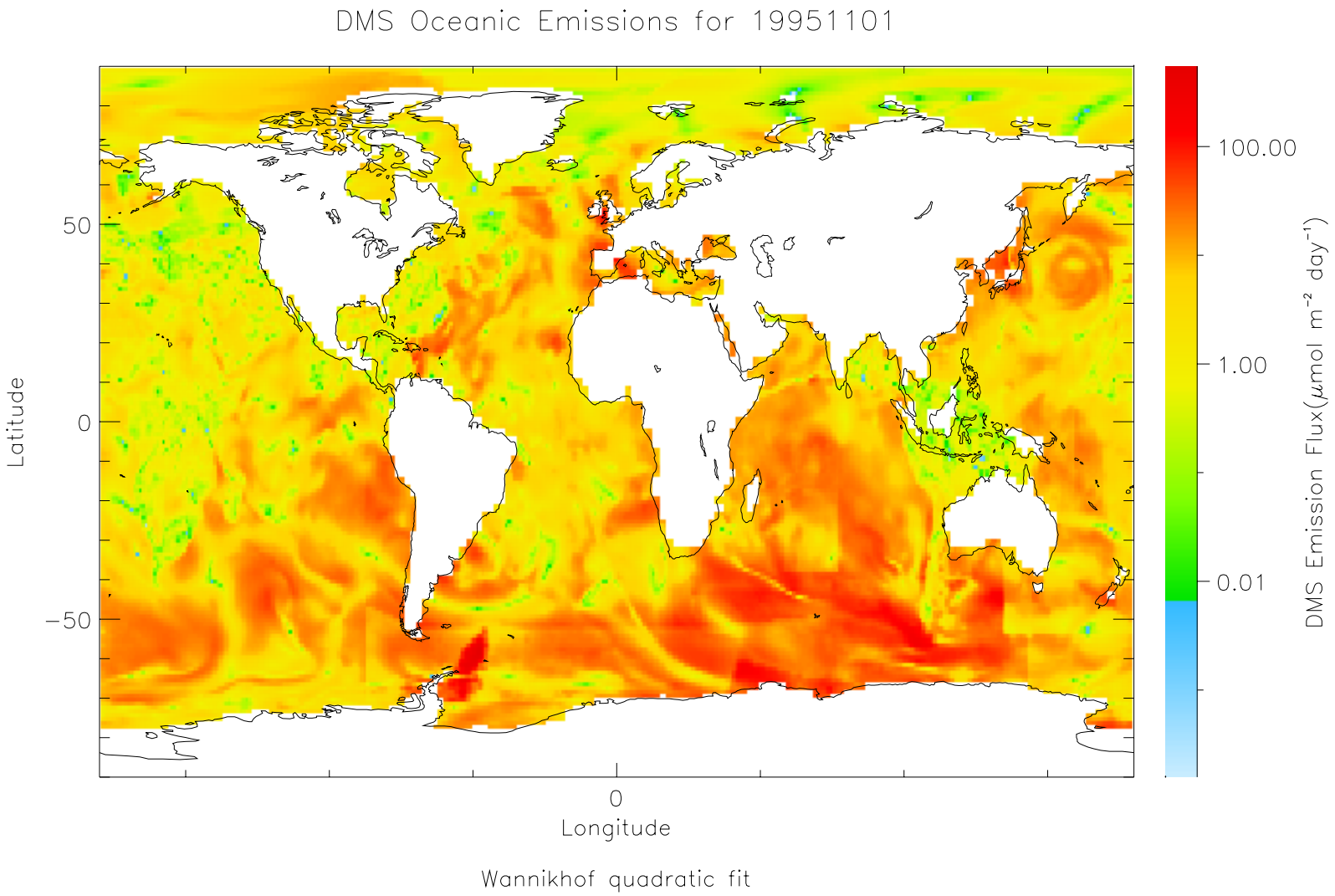
Methodology

- Transformed the cell size to $1^{o} \times 1^{o}$.
- Repeated analysis using the sea-surface temperature.
- Used Wannikhof's quadratic fit and the ECMWF wind speed at 10 m to estimate DMS emissions every 6 hours.


DMS Oceanic concentrations
Latitude
50
0
−50
0
Longitude
10.0
1.0
0.1
DMS Oceanic conc(ηmol L⁻¹)
Data from Kettle et al


DMS Oceanic concentrations
50
0
−50
Latitude
0
Longitude
10.0
1.0
0.1
DMS Oceanic conc(ηmol L⁻¹)
Data from Bates cruise (1995)


DMS Oceanic concentrations
50
0
−50
Latitude
0
Longitude
10.0
1.0
0.1
DMS Oceanic conc(ηmol L⁻¹)
Kettle data merged with Bates


DMS Oceanic Emissions for 19951101
Latitude
50
0
−50
0
Longitude
100.00
1.00
0.01
DMS Emission Flux(μmol m⁻² day⁻¹)
Wannikhof quadratic fit

Sea Salt Aerosol

★ Introduction

Sea salt aerosol is an important component of the total atmospheric aerosol, especially in remote locations (see ACE-1 results).

Atmospheric sea salt particles are generated by the interaction of the wind and waves.

Wind speed, water temperature, air-sea temperature difference, etc. all play a role in aerosol production.

Mechanisms that can generate sea salt aerosol:

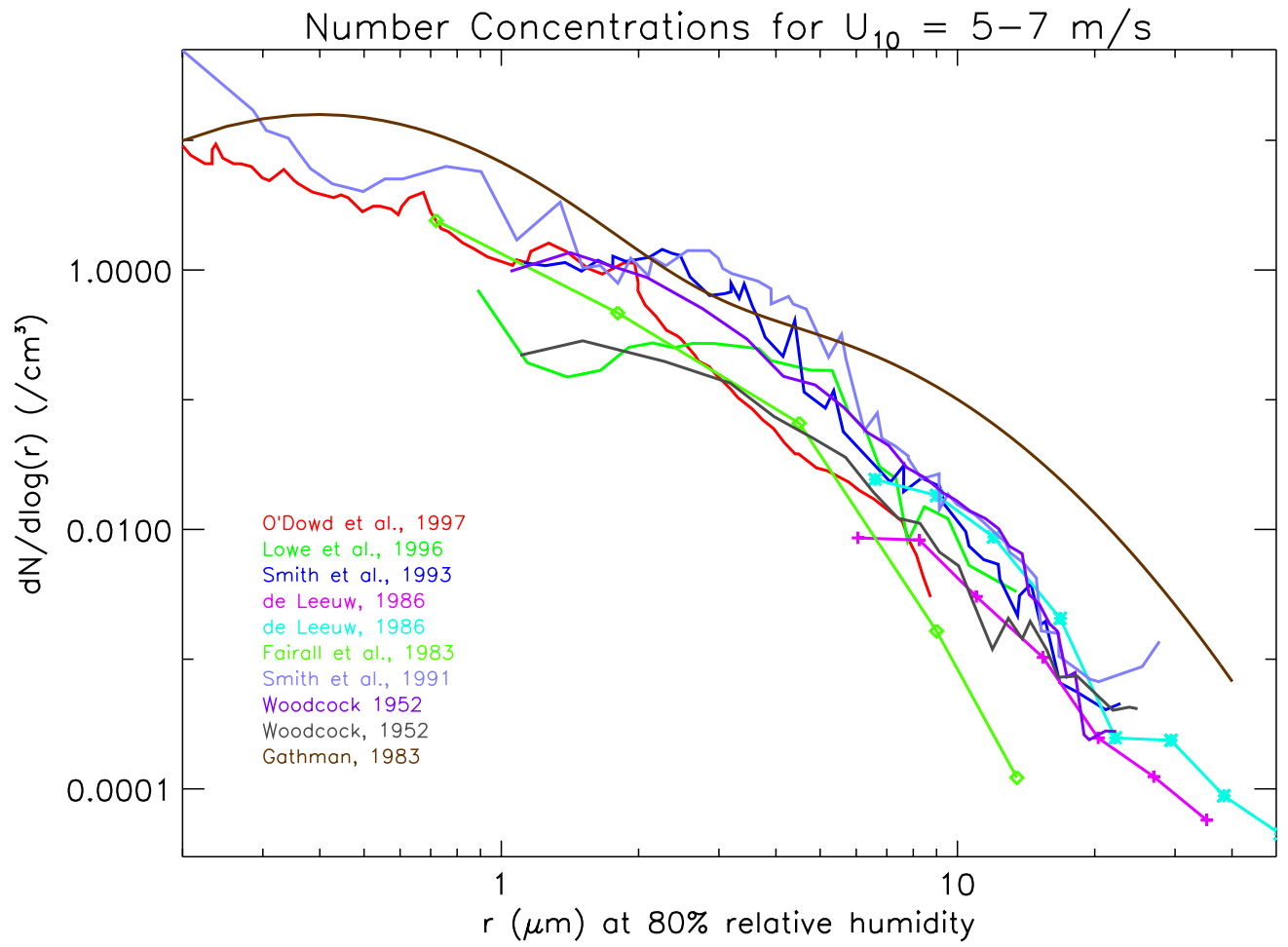
- Bubbles bursting from breaking waves as JET DROPS (bubble cavity is filled in) or as FILM DROPS (bubble cap bursts).
- SPUME DROPS (wave shearing at high wind speeds).

Drops are convected upwards by turbulent eddies.

Sea Salt Aerosol

★ Aerosol number distributions

- # All moments can be calculated from the aerosol number distribution.
- # Figure 1 shows a comparison of various measurements of aerosol number distributions for two ranges of the 10 m wind speed (U_{10}).
- # Values of the radii are at 80% relative humidity, a typical value for the marine environment.
- # Important findings:
  - The trend is similar among the various measurements.
  - The range of the values of the number distributions can be an order of magnitude at similar wind speeds.


Number Concentrations for U_{10} = 5–7 m/s
1.0000
0.0100
0.0001
dN/dlog(r) (/cm³)
O'Dowd et al., 1997
Lowe et al., 1996
Smith et al., 1993
de Leeuw, 1986
de Leeuw, 1986
Fairall et al., 1983
Smith et al., 1991
Woodcock 1952
Woodcock, 1952
Gathman, 1983
1
10
r (μm) at 80% relative humidity

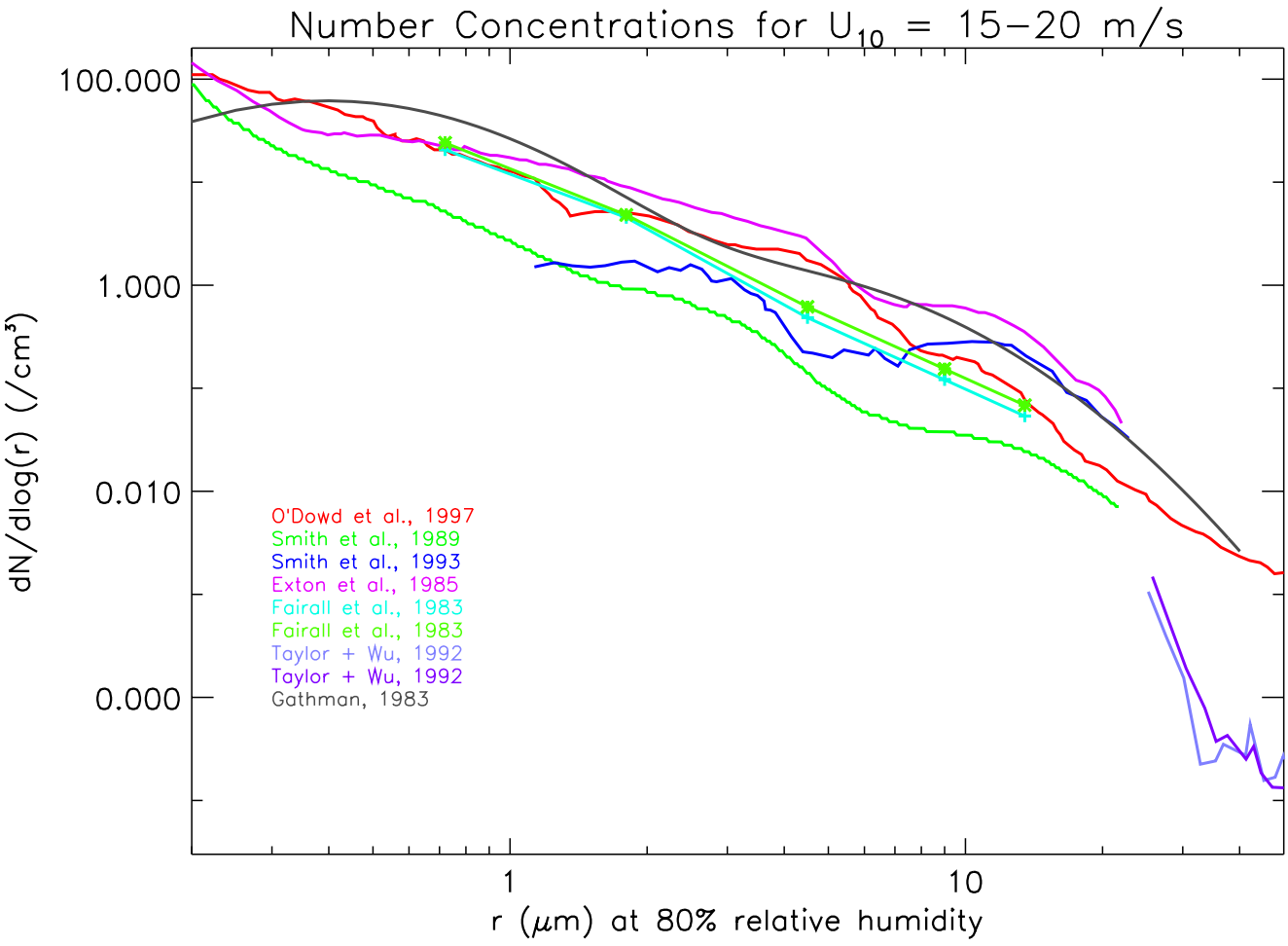

Number Concentrations for U_{10} = 15–20 m/s
100.000
1.000
0.010
0.000
dN/dlog(r) (/cm³)
O'Dowd et al., 1997
Smith et al., 1989
Smith et al., 1993
Exton et al., 1985
Fairall et al., 1983
Fairall et al., 1983
Taylor + Wu, 1992
Taylor + Wu, 1992
Gathman, 1983
1
10
r (μm) at 80% relative humidity

Figure 1

Sea Salt Aerosol

★ Area distributions

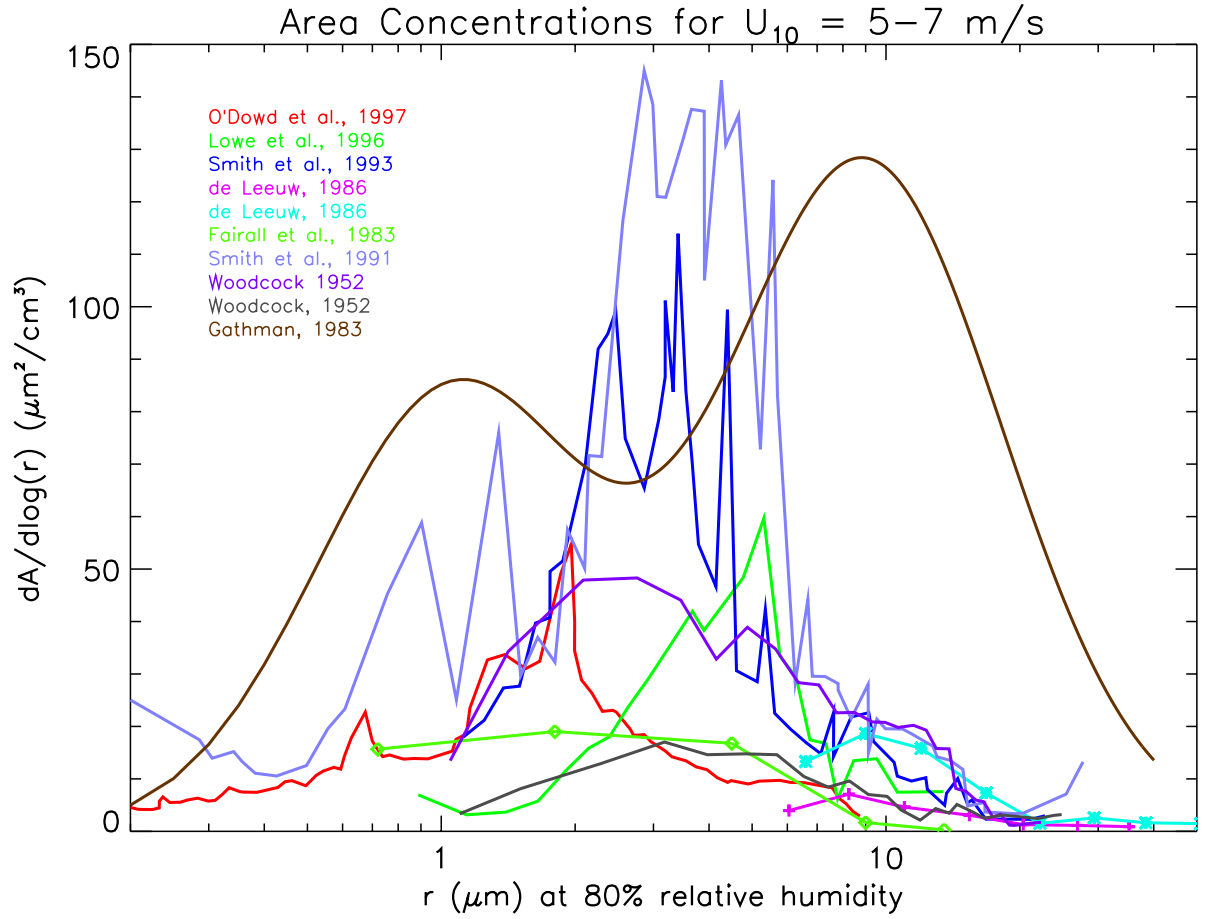
#The surface area of the drops can suppress the production of new particles via nucleation.

#Figure 2 shows the corresponding area distributions for the previous ranges of U_{10}.

#Graphs are on a linear scale and are equal-area plots (the actual area under a curve represents the value between two radii).

#Important findings:

- The main contribution to the aerosol surface area by sea salt is from particles with radii between 1 and 30 um.
- The variability among different measurements can be up to an order of magnitude.
- The main contribution at the lower wind speeds is thought to be from jet drops in the range 1-10 um.
- At higher wind speeds the spume mode increases at larger radii.


Area Concentrations for U_{10} = 5–7 m/s
O'Dowd et al., 1997
Lowe et al., 1996
Smith et al., 1993
de Leeuw, 1986
de Leeuw, 1986
Fairall et al., 1983
Smith et al., 1991
Woodcock 1952
Woodcock, 1952
Gathman, 1983
dA/dlog(r) ($\mu m^2/cm^3$)
150
100
50
0
1
10
r (μm) at 80% relative humidity

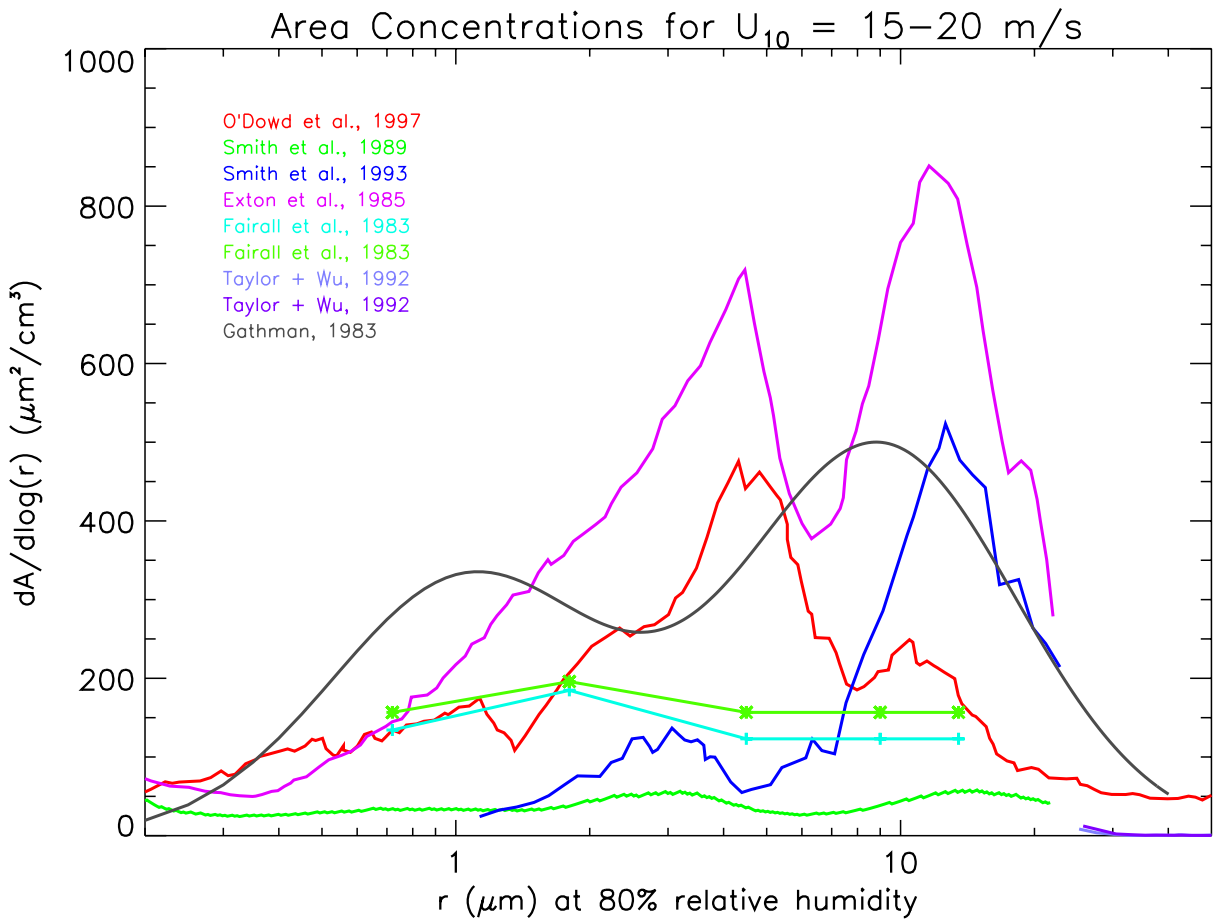

Area Concentrations for U_{10} = 15–20 m/s
O'Dowd et al., 1997
Smith et al., 1989
Smith et al., 1993
Exton et al., 1985
Fairall et al., 1983
Fairall et al., 1983
Taylor + Wu, 1992
Taylor + Wu, 1992
Gathman, 1983
dA/dlog(r) ($\mu m^2/cm^3$)
1000
800
600
400
200
0
1
10
r (μm) at 80% relative humidity

Figure 2

Sea Salt Aerosol

★ Flux of sea salt particles

Is defined as production of particles per unit sea surface area per unit time.

Depends on many factors, the most important being:

- Wind speed.
- Sea surface temperature.
- Wind speed history.
- Fetch.
- Presence of organics.

Is very difficult to measure. Even if measured well, there is usually a high degree of variability among "similar" conditions.`

Sea Salt Aerosol

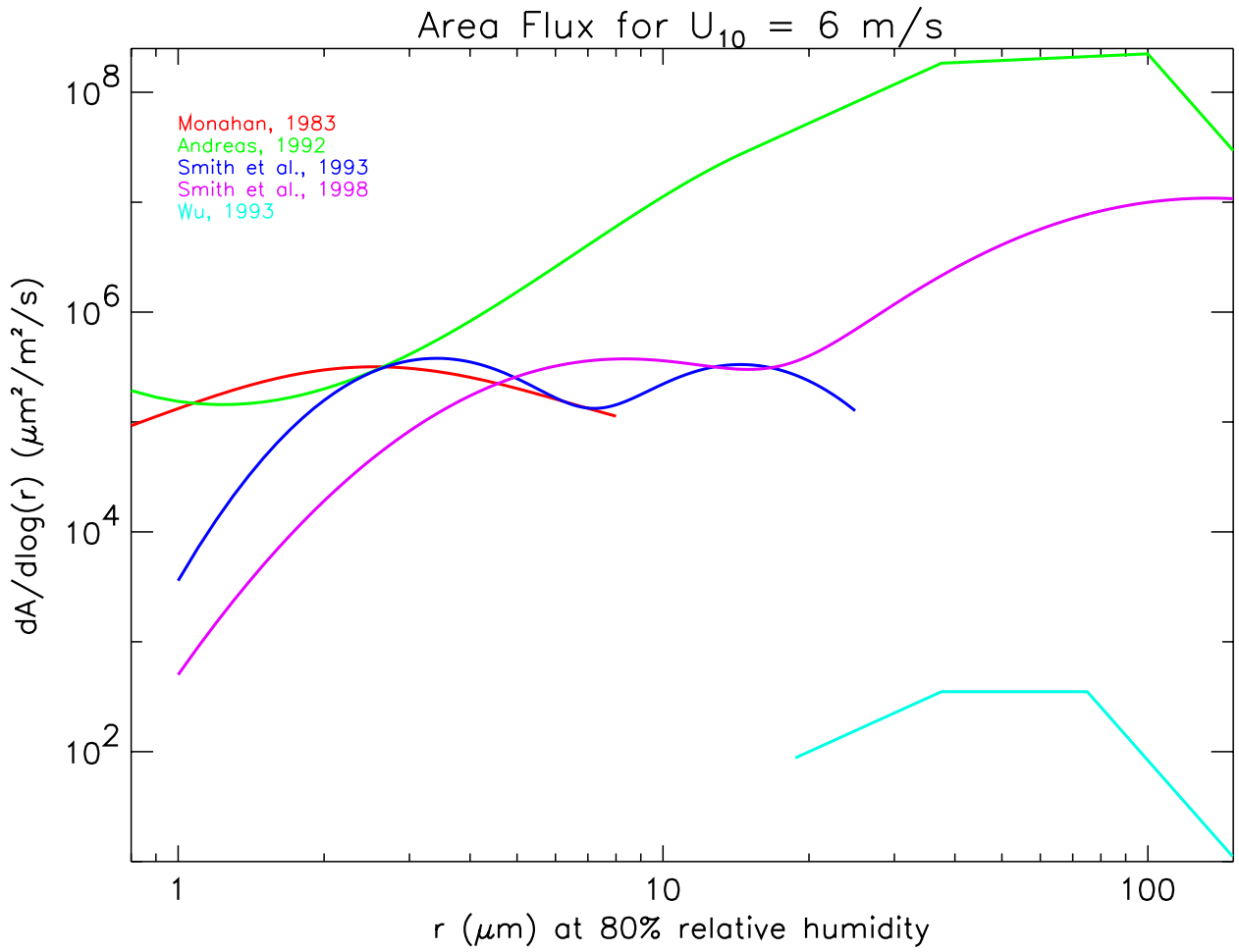
★ FLUX DETERMINATIONS

#The flux of sea salt particles has been predicted by:

- **Laboratory measurements of aerosols produced by breaking waves that have been extrapolated via whitecap coverage to oceanic conditions.**
- **Measurements of concentrations that have been extrapolated to fluxes assuming equilibrium (production = fallout).**
- **Eddy-correlation measurements that can give a "direct" measurement.**
- **Bubble spectra and knowledge of the ratio of drops/bubble.**

#All of these predictions involve questionable assumptions or are difficult to evaluate.

#Various models of the flux of sea salt particles yield fairly different results.


Area Flux for U_{10} = 6 m/s
Monahan, 1983
Andreas, 1992
Smith et al., 1993
Smith et al., 1998
Wu, 1993
dA/dlog(r) ($\mu m^2/m^2/s$)
r (μm) at 80% relative humidity

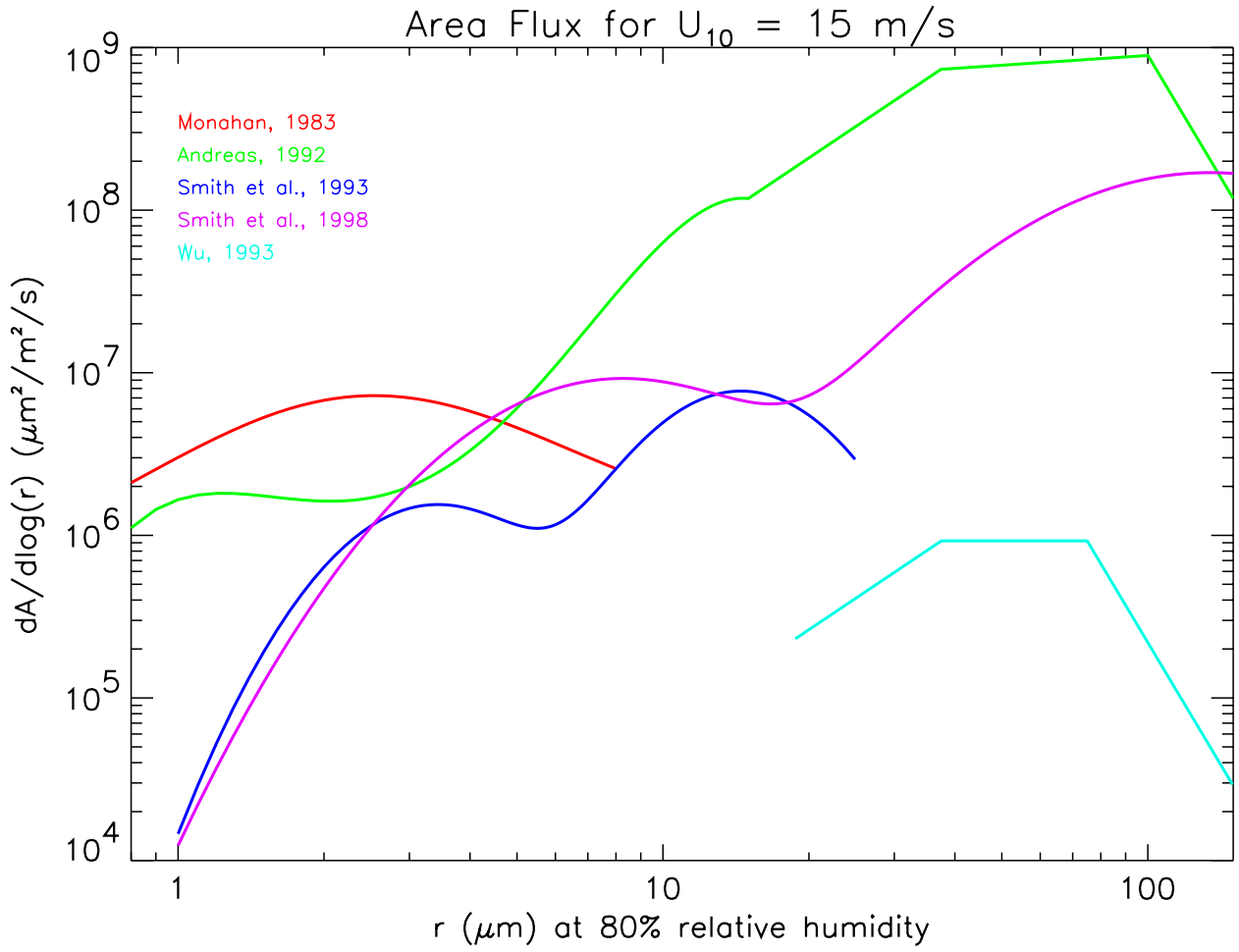

Area Flux for U_{10} = 15 m/s
Monahan, 1983
Andreas, 1992
Smith et al., 1993
Smith et al., 1998
Wu, 1993
dA/dlog(r) ($\mu m^2/m^2/s$)
r (μm) at 80% relative humidity

Figure 3

Mineral Dust Aerosol

★ **Importance**

#Mineral dust aerosols are an important component of the total atmospheric aerosol in arid regions.

#Mineral dust aerosols:

- Provide acid-neutralizing compounds.
- May suppress the production of new particles via nucleation.

★ **Two major models for the flux of wind driven dust are currently available:**

#Tegen et al, 1994, 1995, 1996, 1997.

- Global coverage.
- Less detailed mechanisms.

#Marticorena et al., 1995, 1997.

- Applied to African regions only.
- More detailed mechanisms.

★ **Collaborations with these investigators are in progress.**